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Samples are contained in a temperature-controlled cell that uses a 20-pass optical system with an optical path length of 15.5 m. An H_2O monitor built as an integral part of the instrument measures the H_2O concentration, making it possible to account for a small amount of interference by this gas in the sample. The rms noise-equivalent-concentration of HCN is less than 0.02 ppm. The combined error after accounting for H_2O interference for most dilute samples is less than 0.1 ppm HCN.

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DEVELOPMENT OF A MONITOR FOR HCN IN MOBILE SOURCE EMISSION

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ABSTRACT

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CONTENTS

Abstract		iii
Figures		v
Abbreviations and Symbols		vi
1.	Introduction	1
2.	Conclusions	3
3.	Recommendations	5
4.	Optical Diagram and Layout	6
5.	Gas-Filter Cell and Principles of Detection	11
6.	Electronics and Processing Detector Signal	17
7.	H_2O Monitor	21
8.	Instrument Performance	25
9.	Conversion of the Versatile Gas-Filter Correlation Spectrometer	31
10.	References	34

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FIGURES

Number		Page
1.	Optical Layout of the HCN Instruments	7
2.	Optical Diagram of the Retroreflector-Grid Assembly	8
3.	Side View of the Detector Optics	8
4.	Images Formed by the Multiple-Pass Optics on Mirror C2	10
5.	Diagram of Gas-Filter Cell Assembly	12
6.	Transmission Spectra of HCN, H_2O, NH_3 and C_2H_2	15
7.	Block Diagram of Signal Processing Electronics	18
8.	Optical Diagram of the H_2O Monitor	22
9.	Log-log Plots of the Output Signal vs HCN Concentration for the 5 Different Sensitivity Ranges	26

ABBREVIATIONS AND SYMBOLS

AGC	-- automatic gain control
C_2H_2	-- acetylene
D.R.	-- discrimination ratio, ratio of the concentration of an interfering gas species to the concentration of HCN that produces the same output signal. This ratio may be positive or negative.
GFC	-- gas-filter cell
HCN	-- hydrogen cyanide
lpm	-- liters per minute
m	-- meter
mm	-- millimeters
NH_3	-- ammonia
ppm	-- parts per million (by volume)
RTF	-- relative transmission function of the grating assembly
V	-- voltage
V_c	-- component of amplified voltage at the carrier frequency, 360 Hz.
V_a	-- component of amplified voltage at the modulation frequency, 30 Hz.
V'	-- V_a/V_c (related directly to HCN concentration)
μm	-- micrometer (unit of wavelength)
sec	-- second
dc	-- direct current
Hz	-- cycles per second
rms	-- root mean square

SECTION 1

INTRODUCTION

Certain types of catalytic mufflers used in automobile exhaust systems have been found to produce HCN when the vehicle is tuned fuel-rich. Under some extreme conditions, the HCN concentration in the exhaust may reach unsafe levels as high as 20-50 ppm. Because of the very high toxicity of HCN, it is important that the concentration of this gas be controlled below a harmful level. The chemical process by which the HCN is generated is not fully understood, nor is it possible to predict the HCN concentration resulting from different vehicle operating conditions. It is, therefore, essential that vehicles that are potential producers of high concentrations of HCN be tested so that proper controls and safety precautions can be established.

At the time of the discovery that significant amounts of HCN could be produced, there were no available instruments capable of real-time measurement of the concentration of this gas in vehicle exhaust. This report deals with the development of an infrared instrument for this purpose.

Gas-filter cell (GFC) techniques have been proven by several groups of workers to be quite useful for instruments to measure the concentrations of many different gases that contain much structure in their absorption spectrum. Gas-filter cell instruments depend for their sensitivity and discrimination on a filter that consists of a small cell that contains the gas species to be measured. The infrared spectrum of HCN contains much structure, making this gas a good candidate for GFC techniques.

The first phase of the present project involved a series of tests to investigate the feasibility of an HCN instrument based on GFC techniques and to determine the important parameters and expected performance of such an instrument. The tests were performed on a versatile GFC Spectrometer built previously for the EPA.[1] It is convenient to interchange many of the components in this instrument, such as detectors, gas-filter cells, gratings, filters, etc. It is possible to employ virtually any desired spectral bandpass from 0.3 μm to 14 μm. After the required tests were performed with the versatile GFC spectrometer, it was converted for use as an HCN monitor and returned to the EPA where it has been used for several months. This converted instrument is adequate for most of the measurements to be made with it, although the performance is not as good as can be expected from an instrument designed specifically as an HCN monitor.

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1. Burch, D.E., F.J. Gates, D.A. Gryvnak and J.D. Pembrook. "Versatile Gas Filter Correlation Spectrometer", Prepared by Aeronutronic Ford Corporation under Contract No. 68-02-1227. EPA Report No. 600/2-75-024, June 1975.

The second phase of the project called for designing, building, testing, and delivering three HCN monitors to be used in analyzing exhaust from mobile sources. Results of the tests performed in the first phase served as the basis for the design of these instruments. These three nearly identical instruments employ a narrow infrared spectral interval near 3 μm that contains several sharp absorption features of the HCN absorption spectrum. The same basic GFC technique employed in previous instruments provides good sensitivity, stability and discrimination. With the exception of Section 9, most of the remainder of this report deals with these three instruments.

SECTION 2

CONCLUSIONS

The capability of a gas-filter correlation instrument to measure the concentration of HCN in automotive exhaust has been demonstrated. Although several exhaust gases absorb significantly in the vicinity of the 3 μm HCN band, it is possible to use this absorption band to measure the HCN concentration and to reduce the interference by the other gases to an acceptable level. The most serious interference results from H_2O; some interference also results from CO_2, C_2H_2 and NH_3. Interference by other exhaust gases in their normal concentrations is negligible. Much of the good discrimination against other gases that absorb in the same spectral interval is due to the gas-filter cell; however, the spectral bandpass of the instrument must be selected carefully to obtain adequate discrimination. A cell that contains C_2H_2 is placed in the monitoring beam to reduce further the interference by this gas.

Even with the instruments adjusted for optimum discrimination, there is still excessive interference by H_2O. This interference is accounted for by measuring the H_2O concentration and correcting the output signal by an amount that is related to the H_2O concentration. The relationship between the concentration of H_2O and the interference it produces is determined ahead of time from samples of $H_2O + N_2$. This relationship is not linear, making it impractical to account automatically for the interference with simple electronic circuits as we have done on other instruments built previously. The H_2O concentration is measured by automatically comparing the transmittances over 2 adjacent spectral intervals; one interval near 1.9 μm includes strong H_2O absorption lines, and the other contains only weak lines.

A constant amount of HCN vapor can be kept for several months, and possibly longer, in the small gas-filter-cell with quartz windows fused to a quartz cell body. Less than 0.5 mm of surface of epoxy cement is in contact with the HCN vapor in the small opening used to fill the cell. Epoxy cement or silicone rubber cement cannot be used to seal windows to the cell body because the HCN causes the cement to deteriorate.

Two important features of the GFC assembly contribute to the good stability of the zero setting (the output signal when there is no absorbing gas in the sample cell). A temperature-controlled enclosure maintains the HCN in the GFC at a nearly constant temperature, thus maintaining nearly constant transmittance. The monitoring beam of radiant energy is transmitted through the rotating GFC assembly with essentially no deviation in position or direction of the beam as the assembly rotates. Therefore, the stability of the output signal is almost independent of any unavoidable wobble or shift in the assembly as it rotates. This feature represents an improvement over the mo. e com-

mon type of GFC instrument, which employs a rotating mirror chopper with a stationary GFC. Wobble in the rotating mirror chopper causes deviations in the position and direction of the reflected beam. This instability in the optical beam leads to instability in the zero setting.

The electronic system processes the detector signal in such a way that the output signal varies almost linearly with HCN concentration and is insensitive to small changes in source brightness or detector sensitivity. Good signal-to-noise ratios are made possible by the convenient tungsten-iodide energy source and the liquid-nitrogen-cooled InSb detector. Adequate sensitivity for a 0-1 ppm of HCN full-scale range is achieved by the 15.5 m optical path in the multiple-pass cell. Five separate sensitivity ranges (1,3,10,30, and 100 ppm) make it possible to measure concentrations from approximately 0.05 to 100 ppm.

SECTION 3

RECOMMENDATIONS

The performance of the instruments meets the requirements for the type of measurements for which it is designed. However, results of some of the tests performed on the completed instruments indicate a few design changes that could improve the performance. A few of the changes are discussed below.

Some unexpected instability in the zero-setting has been attributed in part to the non-uniform brightness of the energy source. The source is a tungsten-iodide bulb with a coiled filament; therefore, the image formed on the entrance slit of the grating assembly does not illuminate the slit uniformly. Slight shifts in the optics of the sample cell move the image on the slit and cause slight shifts in the zero setting. If this shift proves troublesome during day-to-day operation, the bulb could be replaced with a Nernst glower, or some other acceptable source that would illuminate the entrance slit more uniformly. A Nernst glower is much less convenient to operate than the tungsten-iodide bulb, but in the spectral interval of interest, the radiance of a Nernst glower is 50%-100% greater than that of the bulb. Therefore, a slightly higher signal-to-noise ratio could also be achieved with a Nernst glower.

The liquid-nitrogen-cooled detector should be mounted so that it is better insulated thermally from the other components. This would probably improve the stability of the zero-setting. Two changes in the sample cell are recommended to reduce errors due to adsorption of HCN on the cell walls. The cell body could be glass lined or made of solid glass, and the volume could be reduced by reducing the diameter. The latter change would reduce the rate that the sample must be flushed to avoid significant reduction in the HCN vapor concentration due to adsorption.

Several of the design features of the instruments are based on the problems related to the real-time measurement of low concentrations of HCN in automotive exhaust. Certain of these design features could be changed for an instrument to monitor the HCN concentration in other kinds of samples.

Sensitivity could be increased by increasing the length of the sample cell. This change would be quite practical if instrument size was not an important factor and if large volumes of sample gas could be used. If C_2H_2 and NH_3 were not present in the sample, the sensitivity to HCN could be improved by employing a wider spectral bandpass shifted to a nearby region where the HCN adsorption is stronger. Sensitivity could also be increased by changing to a narrow spectral interval near 14 μm that includes some very strong HCN adsorption lines. This spectral interval is not practical, however, if the sample contains a high concentration of CO_2, as does automotive exhaust. Discrimination could also be improved by operating the sample cell at reduced pressure; however, this would complicate the gas-handling system.

SECTION 4

OPTICAL DIAGRAM AND LAYOUT

OPTICAL DIAGRAM

Figure 1 is an optical diagram of an HCN analyzer. Radiant energy from the source, a tungsten-iodide bulb, enters the heated enclosure that surrounds the gas-filter cell (GFC) assembly. Lens L1, which serves as an entrance window, forms an image of the source on the 1.4 mm wide by 3.5 mm high slit (slit 1) mounted on the inside wall of the heated enclosure. Flat mirror N1 rotates the converging beam from lens L1 through an angle of 90° so that it passes through the rotating GFC assembly approximately 2 cm below the axis of rotation. The beam alternately passes either through the GFC or the attenuator at a frequency of 30 Hz. A reticle attached to the rotating GFC assembly chops the beam at 360 Hz. Field lens L2 serves as an exit window for the heated enclosure and forms an image of L1 near mirror N3. Mirror N3 (f.l. = 7.5 cm) forms a magnified image of slit 1 next to the front surface of mirror C2 in the sample cell. Lens L3 functions both as an entrance window for the sample cell and as a field lens, imaging mirror N3 near mirror C1.

The path of the beam through the multiple-pass optics is complex; a brief description is given in this section under "Description of the Sample Cell." After passing through the sample cell 20 times, the beam is focused by spherical mirror C6 onto the 0.4 mm wide by 5.1 mm high entrance slit (slit 2) of the grating assembly. The image overfills the slit in the horizontal direction but underfills it in the vertical direction.

The beam of radiant energy entering the grating assembly is rotated 90° by flat mirror G1 and collimated by spherical mirror G2 (f.l. = 38.1 cm). The collimated beam is dispersed by the diffraction grating. Spherical mirror G3 picks off the dispersed energy in the wavelength interval of interest and forms a dispersed image of slit 2 in the grid plane of the retroreflector-grid assembly. A retroreflector with a grid, illustrated in Figure 2, passes the desired spectral interval. The grid has two 7.62 mm high openings cut in it. One of the openings is 0.56 mm wide and the other is 0.94 mm wide. The openings are separated by a 0.20 mm wide metal strip. The beam exiting from the retroreflector assembly follows the reverse path of the beam entering the retroreflector assembly, except the returning beam is displaced vertically. As a result of the vertical displacement of the beam, the returning radiant energy passed by the grid strikes mirror G2 below the incoming beam from mirror G1. Radiant energy in the spectral intervals passed by the grid is focused by spherical mirror G2, forming an undispersed image near the germanium lens LD of the detector optics shown in Figure 3.

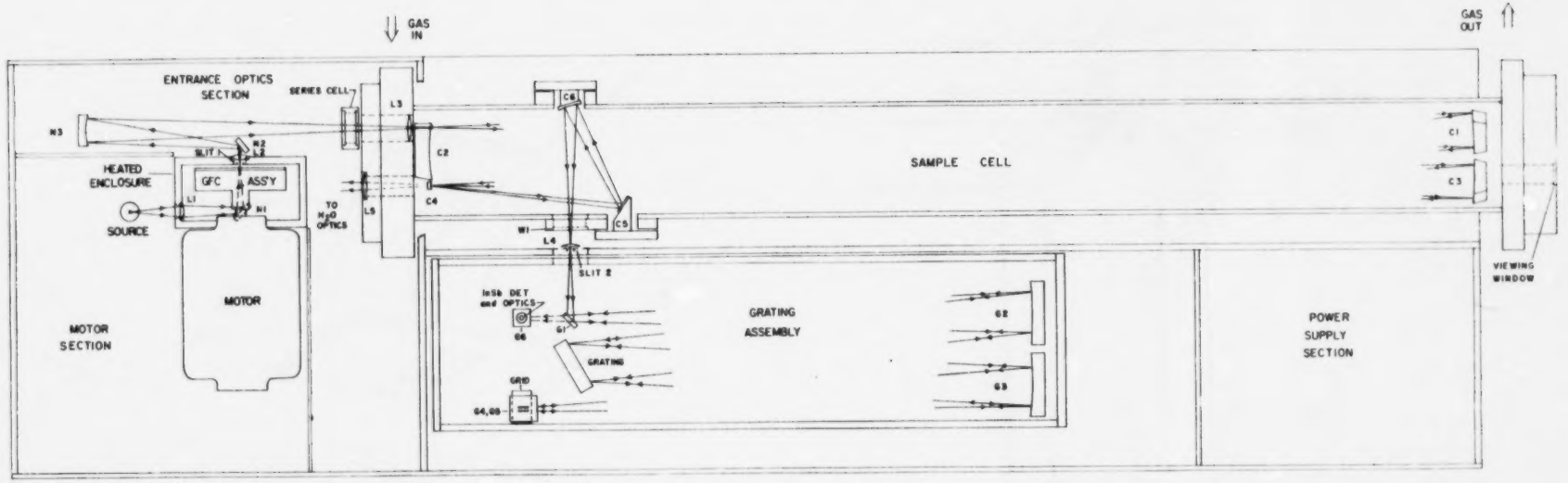

Figure 1. Optical layout of the HCN instruments.

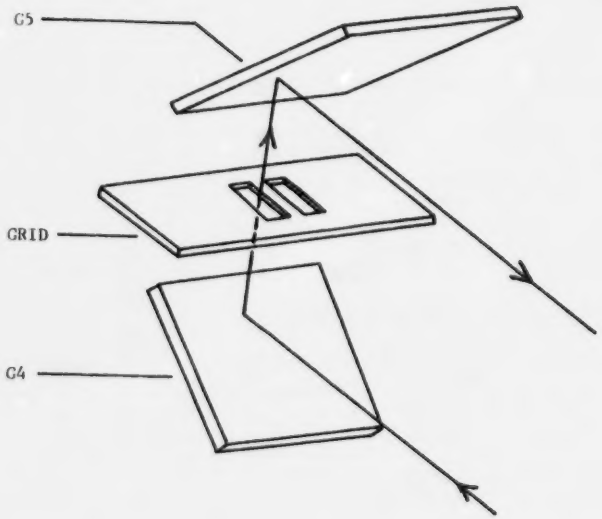

Figure 2. Optical diagram of the retroreflector-grid assembly.

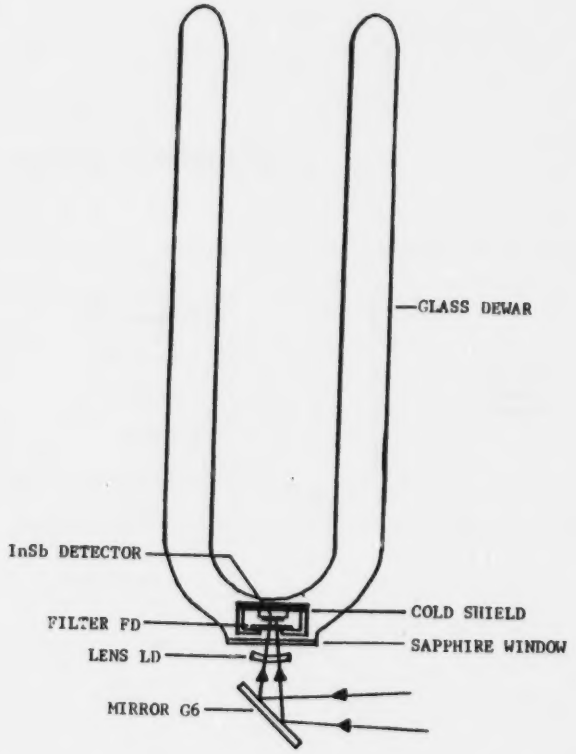

Figure 3. Side view of detector optics.

The converging beam from mirror G2 passes underneath flat mirror G1 and is incident on flat mirror G6, which is mounted 45° from the vertical. After striking mirror G6, the beam travels vertically to the germanium lens LD. This 7 mm focal length lens forms an image of the grating on the 1 mm x 1 mm element of the InSb detector. Filter FD has a spectral bandpass approximately 0.6 μm wide centered near 3 μm. This cold filter reduces the detector noise by reducing the amount of background energy incident on the detector; it also blocks overlapping orders of shorter wavelengths that are passed by the grating assembly.

The phovoltaic InSb detector is mounted in an evacuated glass dewar and is cooled with liquid-nitrogen. The glass dewar has a liquid nitrogen hold time of approximately 3 hours and is potted with RTV in a stainless steel cylindrical housing. (The housing is not shown in Figure 3.) The detector is surrounded by a cold shield, and the bandpass interference filter is mounted in the cold shield. Both of these components are contained in the glass dewar.

The stainless steel grating assembly is spaced off from the baseplate of the instrument by three stainless steel spacers in such a way that stresses in the baseplate will not cause stresses in the grating assembly.

DESCRIPTION OF SAMPLE CELL

The sample cell body consists of an 80-cm long piece of 7.6 cm ID (3.0") stainless steel tubing with flanges welded to each end. The flanges provide support for the various mounts and adjustment plates for the multiple-pass optics. End covers are screwed to each flange and O-rings provide leak-proof seals. Optical path lengths of 337 cm to 2465 cm may be obtained by adjusting the multiple-pass optics; it is intended that the optics remain adjusted to 20 passes, which give a 1553 cm path length.

The cell is maintained at 55°C by a temperature controller that controls the average power dissipated by the heaters. One heater is coiled around the cell body, and a power resistor mounted on each end plate provides additional heat at the ends. The endplates are within ±2°C of the cell body when the cell temperature is stabilized. The temperature near the center of the cell body may be determined by monitoring the output of an iron-constantan thermocouple embedded in the cell body. Foam rubber insulation is wrapped around the cell body and secured with aluminum tape; black foam rubber insulates the ends. The cell is welded to two stainless steel mounting plates which are spaced off the baseplate with 1.27 cm (0.5") thick phenolic spacers to minimize conductive heat losses through the baseplate.

Gas flows into and out of the cell through tubing attached to the 1/4" Swagelok fittings. Gas enters the end of the cell to which mirror C2 is attached and exits the cell at the opposite end, as indicated in Figure 1.

Figure 1 illustrates the multiple-pass optical components mounted inside the sample cell. Spherical mirrors C1 and C3 are cut from the same mirror blank with a 76.2 cm (30") radius of curvature. The distance between the front surfaces of mirrors C1 and C3 and the front surface of spherical mirror

C2 is approximately 76 cm (30"). The magnified image of slit 1 formed by mirror N3 is located adjacent to the front surface of C2. Mirrors C1 and C3 form multiple images of the source on mirror C2. The number of images, and thus the number of cell passes made by the beam, can be set by adjusting the aximuth adjustment screw for mirror C1. Figure 4 illustrates the image pattern on mirror C2 as viewed through the viewing window when the cell is adjusted for 20 passes.

Part of the beam from mirror N3 spills over mirror C1 onto mirror C3, which forms an image of the source adjacent to mirror C2 near lens L5. This energy exits the sample cell after only 2 passes and is use in the H_2O monitor discussed in Section 7.

After passing through the sample cell 20 times, the beam is incident on mirror C4 (focal length = 15.0 cm). This mirror is adjusted to make the beam strike flat mirror C5, which directs the beam to spherical mirror C6. Mirror C6, with a focal length of 6.0 cm, forms an image of slit 1 on slit 2, the entrance slit of the grating assembly. An anti-reflection coated sapphire window is bonded to the exit port of the sample cell. Lens L4 is on a mount attached to the grating assembly and functions as a field lens.

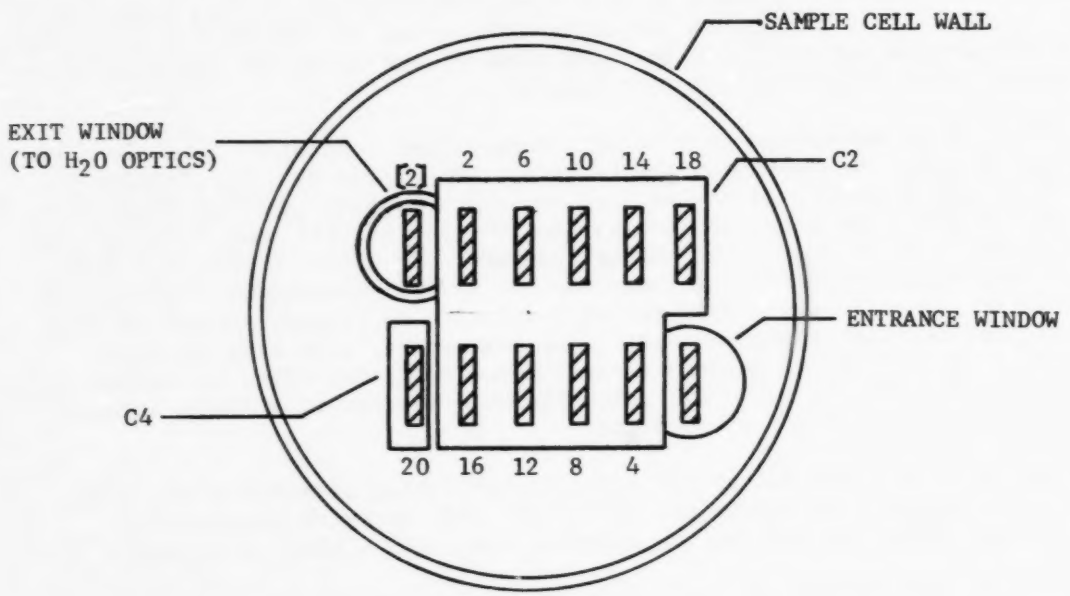

Figure 4. Images formed by multiple-pass cell optics on mirror C2. Numbers by the images indicate the number of passes of the beam through the sample volume when the image is formed.

SECTION 5

GAS-FILTER CELL AND PRINCIPLES OF DETECTION

GAS-FILTER CELL

It was found that gas-filter cells made by us in the past are not suitable for HCN because HCN slowly attacks the epoxy seal, causing it to leak. Thus, the HCN gas-filter cell should not incorporate glass-metal interfaces with epoxy used as a bond. This restriction on the design made fabrication of a leak-proof cell difficult because quartz windows had to be fuzed to the quartz body of the gas-filter cell.

Figure 5 is an assembly diagram of the assembly, which is composed of four parts: the holder, the gas-filter cell, the attenuator windows, and the reticle. The entire assembly is mounted on the shaft of the 1800-rpm hysteresis synchronous motor. As the GFC assembly spins, the beam of radiant energy, located approximately 2 cm below the axis, passes alternately through the attenuator and then through the gas-filter cell at a frequency of 30 Hz. A heated enclosure surrounds the spinning assembly. (Figure 8 in Section 7 is a diagram of the enclosure showing some of the components mounted on or within it.) The temperature of the enclosure, and thus the temperature of the GFC, is maintained at approximately 50°C by a temperature controller that regulates the power dissipated by two power resistors mounted on the enclosure. Insulation is attached to the body of the enclosure, and a phenolic mounting spacer minimizes conductive heat losses to the base plate of the instrument.

The GFC consists of a quartz cell body with quartz windows fused to each side of the cell body. The cell body is made from a disk 5.7 cm in diameter and 6.4 mm thick. The disk is cut approximately in half to form the cell body, and 6 equally spaced radial slots are drilled out of the cell body. Ribs are left between these slots for added strength. Shallow grooves not shown in Figure 5 cut in the cell body interconnect the 6 slots. Another groove connects these grooves with a small hole drilled in the straight edge of the cell body. After the 1.5mm thick quartz windows are fused to the cell body, the 6 radial slots and interconnecting grooves in the cell body form a cavity that contains the HCN. The cell is filled with HCN by attaching a special fitting to the hole drilled in the straight edge of the cell body. The gas flows into the slot volumes via the interconnecting grooves between the slots. After the cell is filled, the hole in the straight edge of the cell body is sealed with epoxy cement.

The attenuator consists of one 1.5-mm thick quartz window and a glass window approximately 0.5-mm thick. The glass window absorbs enough energy to

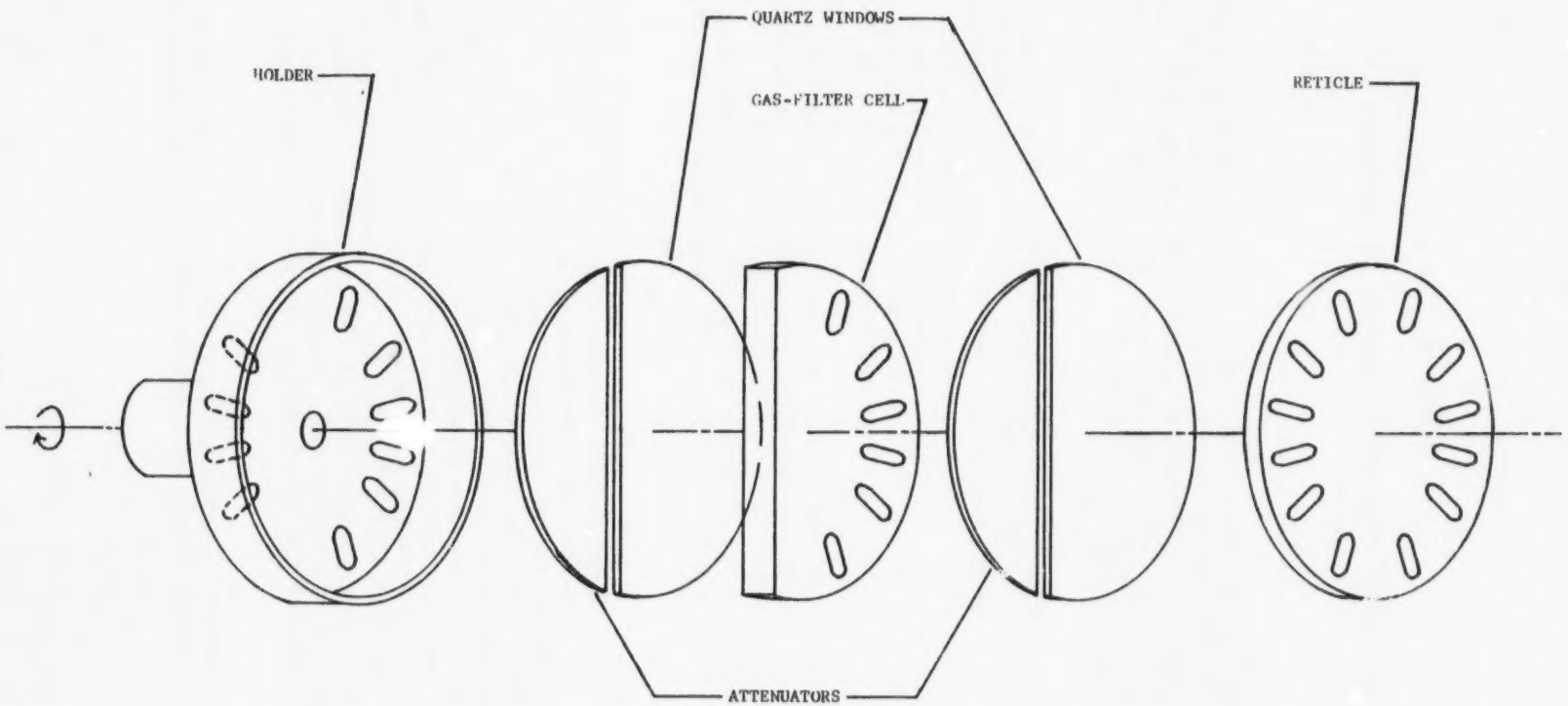

Figure 5. Diagram of the GFC assembly.

make the average transmittance of the attenuator over the spectral region of interest approximately the same as that of the GFC.

The GFC and the attenuator windows are mounted in the black-anodized holder. This 6.9 cm diameter holder has 10 radial slots, 6 slots on the side containing the GFC and 4 slots on the side containing the attenuator. The 6 slots in the GFC are aligned with 6 slots in the holder. Only 4 slots are on the attenuator side of the holder because the GFC, when mounted in the holder, extends into the attenuator side of the holder. The edge of the GFC therefore covers part of the area where the other two slots would normally be. Employing only 4, instead of 6, slots in the attenuator side does not reduce the average value of the chopped energy reaching the detector during each cycle of the GFC assembly because the average transmittance of the attenuator side must be reduced to match the average transmittance of the GFC side. The glass attenuators selected to match the average transmittances of the two halves of the GFC assembly are more transmissive than they would be if 6 slots were used instead of 4.

The disk-shaped reticle is 1.3 mm thick and 6.9 cm in diameter. It has 12 symmetrically placed radial slots that are aligned with the slots in the gas-filter cell and the slots in the holder. As explained in the previous paragraph, no energy passes through 2 of the reticle slots since there are only 10 slots in the holder. Each of the reticle slots is narrower than its corresponding slot in the GFC or the holder, and thus the reticle slots limit the beam as it passes through the gas-filter cell assembly. As the reticle spins at 30 revolutions per second, it chops the beam and produces a strong 360 Hz component on the detector output signal.

PRINCIPLES OF DETECTION

Detailed explanations of the spectroscopic principles of detection and gas-filter correlation principles are given in several reports published by us.[1,2,3] The instrument produces a dc output signal proportional to the

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1. Burch, D. E., F. J. Gates, D.A. Gryvnak and J.D. Pembrook. "Versatile Gas Filter Correlation Spectrometer", Prepared by Aeronutronic Ford Corporation under Contract No. 68-02-1227. EPA Report No. 600/2-75-024, June 1975.

2. Burch, D.E., and D.A. Gryvnak. "Infrared Gas-Filter Correlation Instrument for In-Situ Measurement of Gaseous Pollutants." Prepared by Philco-Ford Corporation for EPA under Contract No. 68-02-0575. EPA Report No. EPA-650/2-74-094. Also, Burch, D.E., and D.A. Gryvnak. "Cross-Stack Measurement of Pollutant Concentrations Using Gas-Cell Correlation Spectroscopy." Chapter 10 of Analytical Methods Applied to Air Pollution Measurements, Stevens, R.K. and W. F. Herget, (eds) Ann Arbor, Ann Arbor Science Publishers Inc., 1974.

3. Burch, D. E., Gates, F. J., Gryvnak, D.A., and J. D. Pembrook. "Versatile Gas-Filter Correlation Spectrometer." Prepared by Aeronutronics Ford Corporation for EPA under Contract No. 68-02-1227. EPA Report No. EPA-600/2-75-024, June 1975.

concentration of HCN in the sample cell. When no HCN is in the sample cell, the two halves of the gas-filter cell assembly cycle are electronically and optically balanced to produce zero output. When HCN is added to the sample cell, the gas absorbs a fraction of the energy that passes through the attenuator when it is in the beam. However, when the gas-filter cell is in the beam, the HCN in the GFC absorbs most of the energy at wavelengths where the HCN in the sample cell absorbs. Therefore, the addition of HCN in the sample cell effectively decreases the energy incident on the detector when the attenuator is in the beam more than it reduced the energy when the GFC is in the beam. Thus, the detector signal is chopped at 360 Hz with a modulation at 30 Hz, the rotational frequency of the gas-filter cell. The detector signal is processed by the electronics to produce a dc output signal proportional to the fractional modulation of the energy incident on the detector, and thus to the concentration of HCN in the sample cell.

Any absorbing gas species other than HCN in the sample cell will not produce a 30-Hz modulation if there is no correlation between the spectral structure of the gas and the spectral structure of the HCN in the gas-filter cell. When there is no correlation between the spectral structures, the gas absorbs exactly the same fraction of the energy passing through the gas-filter cell as that passing through the attenuator. Thus, under this idealized condition, no 30-Hz modulation is produced and there is no interference in the output signal by the gas. Of course, the instrument can not operate properly if the absorbing gas absorbs a large fraction of the radiant energy incident on it. Unfortunately, there is usually a small amount of correlation between the spectral structures of the gas species to be detected and another gas that absorbs in the same spectral region.

Figure 6 shows superimposed spectra of HCN and three other automotive exhaust gases that absorb in the spectral region of interest. Reducing interference by these three gases, H_2O, C_2H_2 and NH_3, while maintaining good sensitivity to HCN has been the most difficult problem in the HCN analyzers. The unpublished curves in Figure 6, obtained with a Fourier Transform Interfermometer by Dr. Herget[4], show spectral features for each gas. Careful consideration of these features is required in order to optimize the discrimination. The dashed curve represents the absorption spectrum for 4.75 m of atmospheric path at 20°C and is labelled "H_2O" since H_2O is the only significant atmospheric absorber in this spectral region. The other three curves are spectra of the three gases indicated in a 10-cm absorption cell at 20°C. The HCN sample consisted to 6650 ppm of HCN in N_2 at 1-atm total pressure. The NH_3 and C_2H_2 samples were pure at pressures of 40 torr and 20 torr, respectively.

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4. Herget, Dr. William F., Environmental Protection Agency, Research Triangle Park, N.C., 27711 (Private communication)

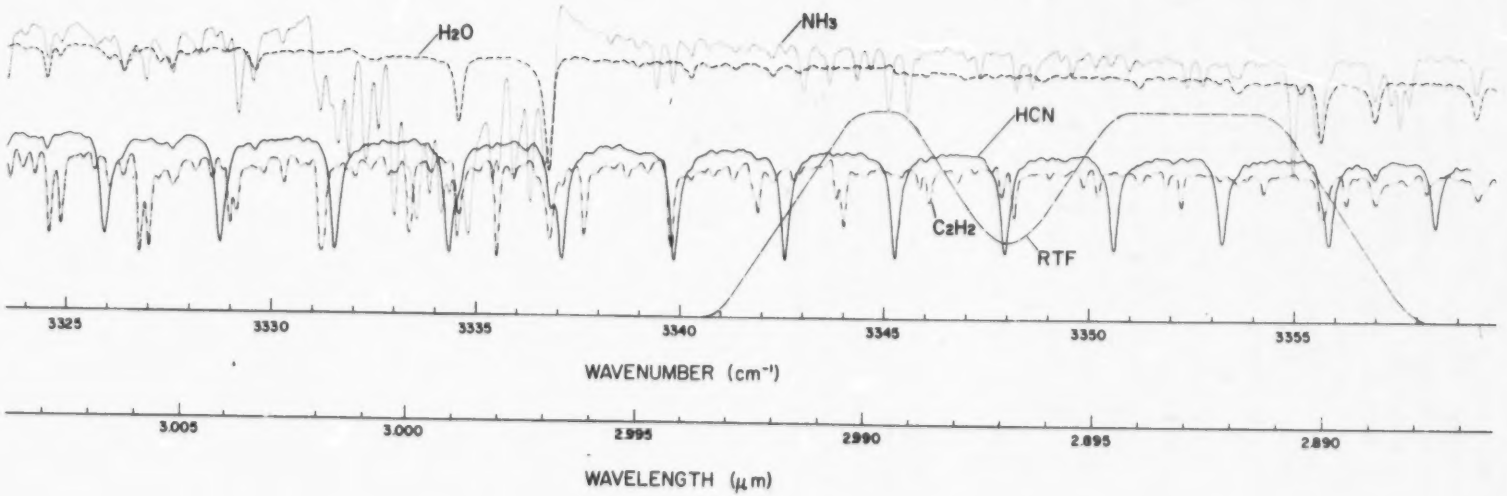

Figure 6. Transmission spectra of HCN, H_2O, NH_3 and C_2H_2. The relative transmission function of the grating assembly is indicated by the curve labelled RTF.

The "relative transmission function," RTF, of the retroreflector-grid assembly is illustrated graphically in Figure 6. This function is determined by the width of the entrance slit, the widths and spacings of the slots in the grid (see Figure 2), and the dispersion in the plane of the grid. An opaque strip between the two grid slots causes the minimum in the relative transmission function near 3348 cm^{-1}. Reducing the relative transmission near 3348 cm^{-1} greatly reduces the interference by C_2H_2. If the complete spectral interval were employed with approximately the same relative transmission over the entire interval, the C_2H_2 would interfere positively in the measurement of HCN concentration and would thus cause the instrument to indicate too high of a concentration of HCN. Blocking out some of the energy near the almost coincident HCN and C_2H_2 lines close to 3348 cm^{-1} reduces the positive correlation between the spectral structures of these two gases.

The 1/3 - atm of C_2H_2 in the series cell further reduces the interference by C_2H_2 in the sample. The gas in the series cell absorbs much of the radiant energy from the monitoring beam at wavelengths where this gas absorbs strongly. Thus, the absorption by the C_2H_2 in the sample cell is greatly reduced. The series cell is so-named because it is placed optically "in series" with the sample cell and the monitoring beam passes through it at all times. By contrast, the gas-filter cell is only in the monitoring beam during half of each revolution of the gas-filter cell assembly.

The spectral bandpass was selected experimentally to minimize interference by H_2O, the automotive exhaust gas that interferes most. Ammonia (NH_3) also absorbs within the spectral interval passed by the instrument, but interference by this gas is not serious because of the small amount of correlation between the spectral structures of NH_3 and HCN.

SECTION 6

ELECTRONICS AND PROCESSING OF DETECTOR SIGNAL

The electronics process the signal from the detector and produce a dc voltage that is proportional to the concentration of HCN in the sample gas. The relationship between the output voltage and the HCN concentration is determined by calibrating the instrument with samples of known concentration. A block diagram of the electronics used to process the detector signal is shown in Figure 7. The 360-Hz component of the signal from the detector serves as the carrier for the 30-Hz component that is to be measured. The 30-Hz component of the detector signal resulting from any 30-Hz variation of radiant energy on the detector that is not also chopped at the carrier frequency is rejected by the electronics. The electronics consist basically of two demodulators in series. The first demodulator operates at the carrier frequency, 360 Hz; the average output of this demodulator is proportional to the amount of radiant energy chopped at 360 Hz. If the chopped energy incident on the detector is also modulated at 30 Hz, the 30-Hz component of the output signal from the 360-Hz demodulator is proportional to the modulation. This 30-Hz component then passes through a series of gain controls and amplifiers to the 30-Hz sychronous demodulator. The output of the 30-Hz synchronous demodulator is proportional to the 30-Hz modulation of the 360 Hz signal, and thus to the concentration of HCN in the sample gas. The reference signal for the 30-Hz synchronous demodulator is supplied by the 30-Hz reference pick-up mounted on the heated enclosure where it senses the rotation of the GFC assembly.

When H_2O is in the sample gas, the 30-Hz signal also contains a component due to the H_2O. This interference is accounted for analytically from the output of an H_2O monitor described in Section 7 that produces a dc signal proportional to the H_2O concentration. Several instruments built previously by us have employed "H_2O Correction" circuitry that used the output of the H_2O monitor to produce an electrical signal in the electronics that process the signal from the detector in the main channel. This electrical signal was proportional to the H_2O concentration and was adjusted to correct automatically for the interference by H_2O in the main channel. However, this correction circuitry can not be used in the same manner in the HCN analyzers because the interference by H_2O is not proportional to the H_2O concentration. Therefore, it is necessary to read the H_2O concentration from the H_2O monitor and determine the correction from a curve determined experimentally for each unit.

A time constant switch mounted on the main electronics card makes it possible to select an electronic time constant of 0.3, 1, 3 or 10 sec. The

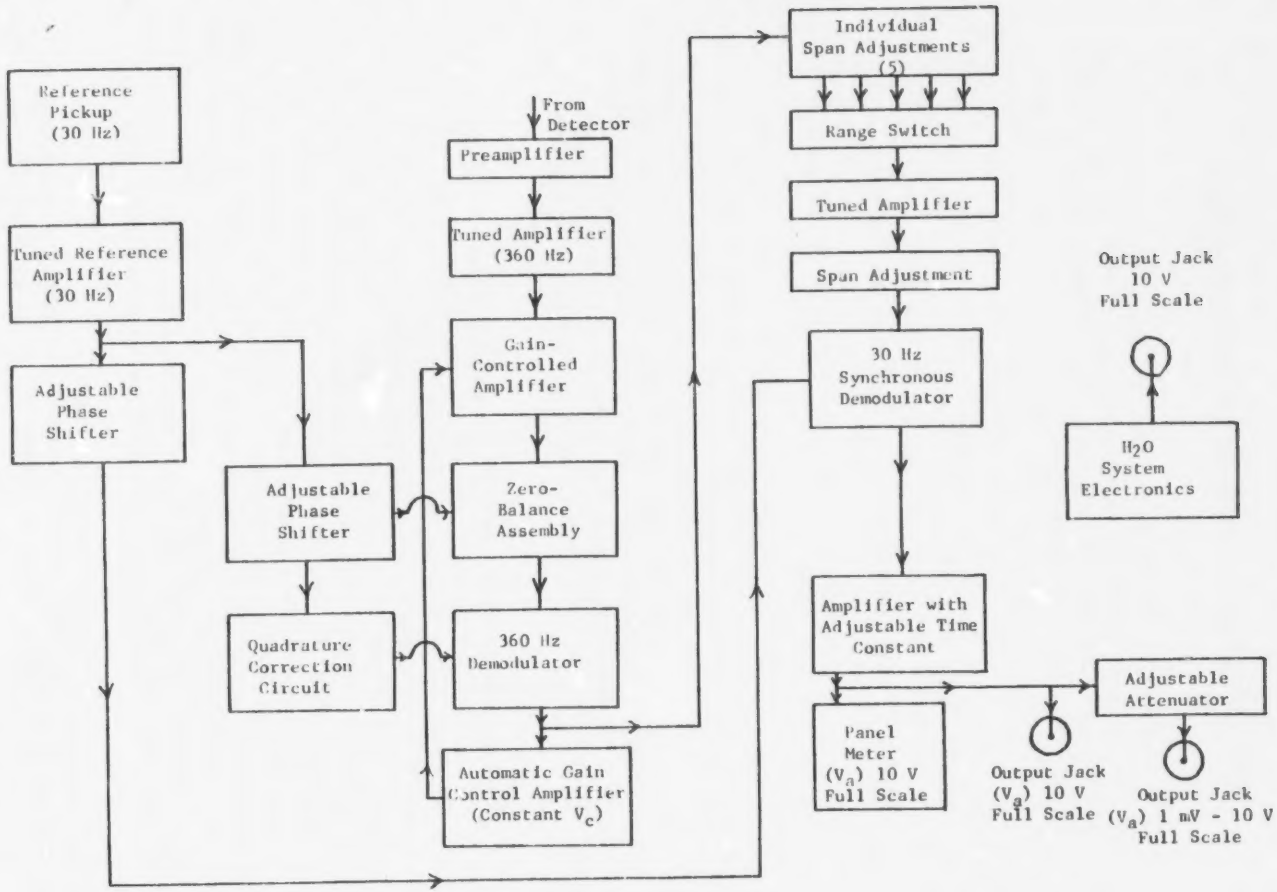

Figure 7. Block diagram of the signal-processing electronics.

main output signal can be determined from a panel meter or from either of two output jacks. A signal that corresponds to a full-scale reading of the panel meter produces a 10 volt dc signal on one of the output jacks. The corresponding full scale reading for the other output jack can be adjusted from less than 1 mv to 10 v. Thus, the instrument can be used with a wide range of recorders or meters, provided the input impedance is sufficiently high.

During the normal mode of operation it is desirable that the output signal be proportional to the ratio, $V_a/V_c = V''$, where V_a is the average demodulated 30-Hz component of the detector signal and V_c is the 360-Hz component of the detector signal. The instrument calibration relates the HCN concentration of the sample gas to V', and it is desired that this relationship be independent of source brightness, detector sensitivity, etc. During the normal mode of operation, V_c is maintained at a constant value by the automatic gain control (AGC) circuits. If, for example, the signal from the photodetector decreases because of dirt on a window or a decrease in source brightness, the AGC increases the amplification of both the 360-Hz signal and the 30-Hz signal by the same factor. Therefore, V' is kept directly proportional to the output, V_a, and maintains a constant relationship with the HCN concentration.

The 30-Hz reference pickup consists of a light-emitting diode (LED) and a small phototransistor. Aluminum tape is wrapped around half the circumference of the reticle, and the other half is black. As the GFC assembly spins at 1800 rpm, light from the LED is reflected by the aluminum tape but not by the black area. The reflected light is sensed by the detector and produces a 30-Hz signal. The amplifier for the 30-Hz reference pickup is tuned and contains an adjustable phase shifter to produce a "clean" signal with the proper phase for the 30-Hz synchronous demodulator.

The zero-balance assembly electronically accounts for any misbalance between the two halves of each cycle of the GFC assembly when there is no HCN in the sample cell. This electronic assembly would not be required if it were practical to maintain a perfect optical balance between the two halves. Approximately ± 10 percent variation in the transmittance through either of the two halves of the cycle can be accounted for by this electronic zero-balance assembly. The assembly changes the amplification ahead of the 360 Hz demodulator during one of the two halves of the GFC assembly cycle. A signal from the 30-Hz reference pickup switches the zero-balance assembly between the two different gains with the proper phase. The difference in the gains between the two halves is adjusted with the "zero" potentiometer mounted on the top of the instrument.

Five ranges of sensitivity are provided: 1,3,10,30, and 100 ppm full scale. The gain in each range can be adjusted independently over a factor of approximately 5 if different sensitivities are desired. A five-position switch mounted on the top of the instrument makes it convenient to change from one range to another. An additional potentiometer mounted on the main electronics card is also provided to change the gain of all 5 ranges simultaneously by the same factor. This single adjustment is usually adequate for making small corrections in the span calibration.

A four-position switch mounted on the main electronics card makes it possible to use the panel meter to monitor quantities other than the output signal. The 30-Hz reference signal and the average carrier voltage, V_c, can be checked with this meter to see if they are in the correct operating range. When the selector switch is in the "signal-in" position, the meter reads the level of the signal going into the 360 Hz synchronous demodulator. With the selector switch in the "signal out" position, the meter reads the level of the output signal. The signals on the output jacks are not affected by the position of the selector switch.

SECTION 7

H_2O MONITOR

OPTICAL

The H_2O monitor produces a dc voltage that is proportional to the concentration of H_2O in the multiple-pass sample cell. The H_2O concentration is determined by comparing the transmission of the sample at two wavelengths, one in the region of strong H_2O absorption near 1.9 μm and one in a nearby region of weak H_2O absorption.

The optical components employed by the H_2O system are shown in Figure 8. The bottom portion of the figure is a side view of the H_2O detection system optics, and the top portion of the figure is a top view. The heated enclosure for the GFC assembly is shown. Components mounted inside the enclosure are shown as they would be viewed with the top off, for the top view, and the back wall off, for the side view. Detectors DA and DB and their associated filters, FA and FB, are mounted on an aluminum block, which is mounted in the top section of the heated enclosure. The spinning GFC assembly, which is mounted on the motor shaft inside the heated enclosure, is also shown in the figure.

When the sample cell is set at 20 passes, mirror C3 forms an image of the source adjacent to mirror C2 and next to lens L5. (See Figure 4) This energy exits from the sample cell and is used in the H_2O detection system. Lens L5, with a focal length of 10.1 cm, forms an image of C3 near lens L6. The combination of flat mirrors H1 and H2 raises the beam of energy exiting from the sample cell by 5.7 cm and directs the beam into the top section of the heated enclosure. Lens L6, with a focal length of 3.8 cm, forms images of slit 1 on detectors DA and DB.

Detectors DA and DB have photoconductive PbS elements, 4 mm x 4mm, that are mounted on a small aluminum block as shown in Figure 8. Filter FA acts as a dichroic beam-splitter, transmitting a narrow spectral interval in the region of strong H_2O absorption near 1.9 μm. The wavelengths not transmitted by filter FA are reflected to filter FB, which transmits a narrow spectral interval of weak H_2O absorption. The gains of the preamplifiers are adjusted so that the 360 Hz signals from the two detectors are equal when no absorbing gas is in the sample cell. It is apparent that the addition of H_2O to the sample cell would reduce the amount of energy incident on detector DA more than it would reduce the amount of energy incident on detector DB. The resulting difference in the detector signals is proportional to the H_2O concentration.

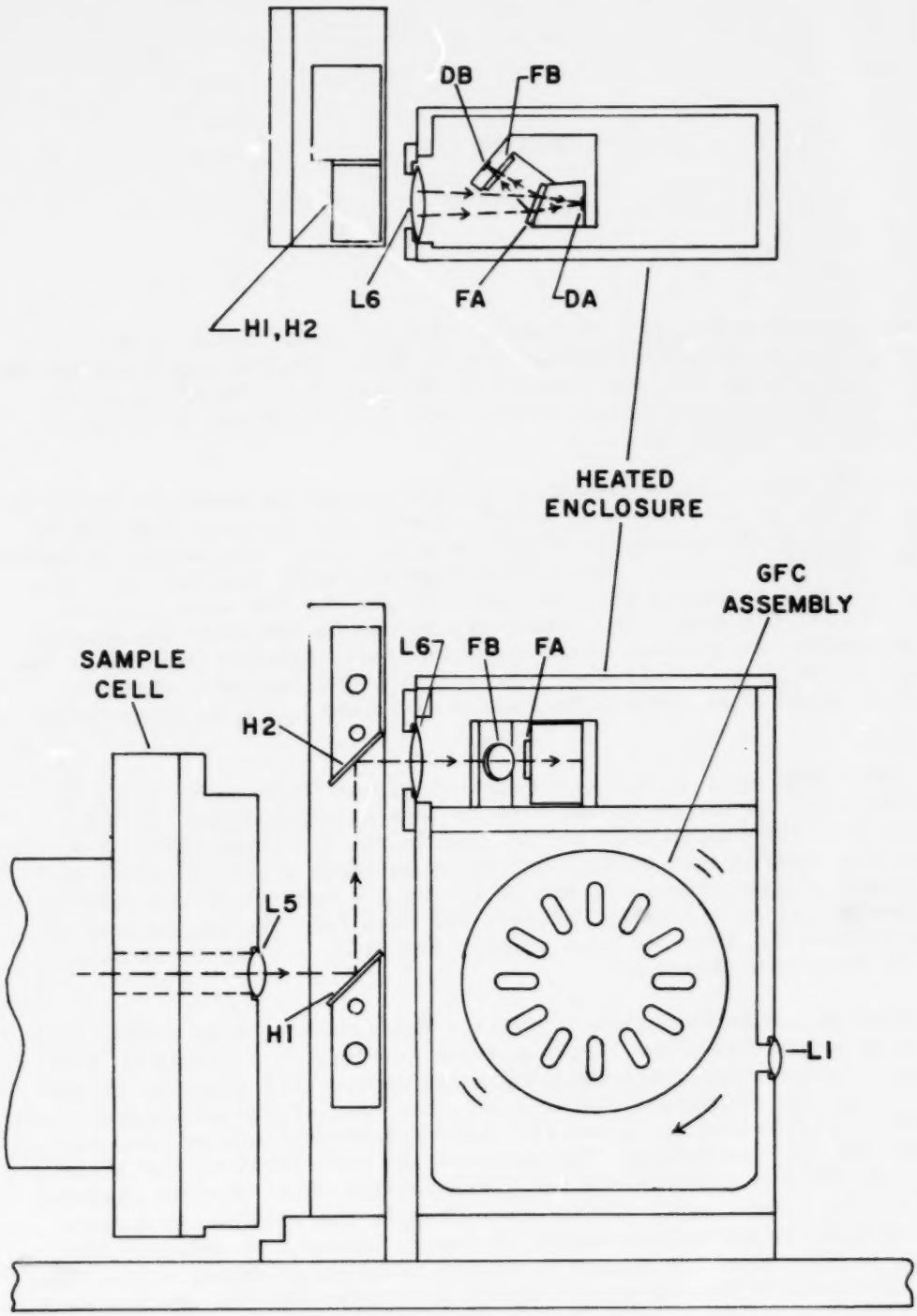

Figure 8. Optical diagram of the H_2O monitor.

Since small variations in the temperatures of the detectors and filters can produce drift in the zero-reading of the H_2O monitor, these components are maintained at approximately 50°C by the heated enclosure. We have found from experience with similar instruments that this 2-detector type of monitor is quite adequate for the present purposes. By employing two fixed filters and two detectors, it is possible to keep the optics of the H_2O monitor relatively simple and not employ any moving optical components that are not required by the HCN channel.

SIGNAL PROCESSING

The bias voltage for detectors DA and DB is provided by a ± 15 Vdc power supply used with the main electronics. A separate preamplifier amplifies the output of each detector, and the outputs of both preamplifiers are fed into a difference amplifier. When the sample cell is free of any H_2O, the monitor is zeroed by adjusting the outputs of the preamplifiers so that they are equal, thus producing a zero input to the difference amplifier. This is done with a fine zero control that is mounted on the front panel of the instrument and a coarse zero control that is mounted on the H_2O electronics card. The addition of H_2O to the sample cell creates a misbalance between the signals from the two preamplifiers and results in a signal from the difference amplifier. This signal passes through a tuned amplifier and is then demodulated to produce a dc voltage that is proportional to the H_2O concentration. A reference signal for the synchronous demodulator is obtained from the output of the preamplifier for detector DB.

A variable-gain amplifier makes it possible to adjust the "span" so that full-scale readings of the panel meter can be made to correspond to H_2O concentrations between approximately 1 percent and 10 percent. An output jack mounted on the instrument can be used to monitor the H_2O output signal. The H_2O output signal is displayed on the panel meter mounted on the top of the instrument when the H_2O button is pressed.

An automatic gain control (AGC) circuit is employed so that the amplified difference signal is nearly independent of slight changes in such things as source brightness or dirt on windows that would change the amount of energy incident on both detectors by about the same factor. The AGC circuit maintains the signal from the preamplifier for detector B at a constant level. For example, if a change in the optics occurs that would ordinarily decrease the detector signal, the bias voltage is increased automatically to compensate for the decrease in radiant energy. The bias voltages for both detectors are increased by the same factor; therefore, to a good approximation, the change in bias voltage increases the outputs of both detectors by the same factor. It follows that a given output of the difference amplifier represents a certain fractional difference in the outputs of the two preamplifiers. This difference can then be related to the H_2O concentration and is nearly independent of small changes in source brightness, dirt on windows,etc.

The amount of H_2O interference is different for each of the 3 units; therefore a separate curve relating the interference error to the output of the H_2O monitor is provided for each unit. As a typical example, the maximum H_2O interference on Unit 2 corresponds to 0.7 ppm of HCN and is produced

by approximately 1.5% H_2O. At either higher or lower concentrations, the H_2O interference is less. Because of the non-linear relationship between the H_2O interference and the concentration of this gas, it is not possible to use the H_2O "Correction" circuitry originally designed and built to account automatically for the H_2O interference. Instead, the H_2O concentration is determined from the output signal of the H_2O monitor, and the correction determined from the interference curve is applied analytically to the output signal of the HCN channel.

SECTION 8

INSTRUMENT PERFORMANCE

SENITIVITY AND CALIBRATION

Hydrogen cyanide vapor adsorbs readily to the surfaces of many types of containers, including metal tubing and the stainless steel sample cell. The adsorption, and subsequent desorption, can cause serious errors in sampling dilute mixtures of HCN + N_2. A larger fraction of the HCN can adsorb on the container walls when the concentration is low than when it is high. This makes it difficult to make accurate dilute mixtures that can be used reliably as standards to calibrate instruments. This difficulty was partially overcome in calibrating the HCN instruments by using sample path lengths much shorter than the 15.5 m path length at which the instrument is to be used. The output signal of the instrument is proportional to the product of path length and HCN in concentration. Therefore, we were able to use higher concentrations of HCN in the standard HCN + N_2 mixtures. The lowest concentration of the standard samples was approximately 500 ppm.

Two short calibration cells (1.5 cm and 6.0 cm) were placed in the monitoring beam near the series cell (see Figure 1), and the multiple-pass cell was adjusted to 4 passes. The multiple-pass cell and the short cells were maintained near 50°C, normal operating temperature of the multiple-pass cell. All standard calibration samples were maintained at essentially 1.00 atm and were flushed through the cells long enough that adsorption on the walls did not reduce the vapor concentration significantly when the output signal was measured.

Figure 9 shows typical log-log plots of the output signals for the 5 different sensitivity ranges vs the equivalent concentration at the normal path length of 15.5 m. A 10 volt output signal corresponds to full-scale deflection of the panel meter. When the concentration is lower than approximately 10 ppm, the output signal is directly proportional to the concentration. An accurate set of curves is provided for each instrument to relate HCN concentration to the output signal for the 30 ppm and 100 ppm ranges.

NOISE AND DRIFT

Most of the noise on the output signal originates in the detector and preamplifier when the optical components are clean and aligned properly. If some of the optical components, particularly the multiple-pass mirrors, are not aligned properly, additional noise may result from vibrations in the optics. The noise level corresponds to the same concentration of HCN regardless of the sensitivity range employed.

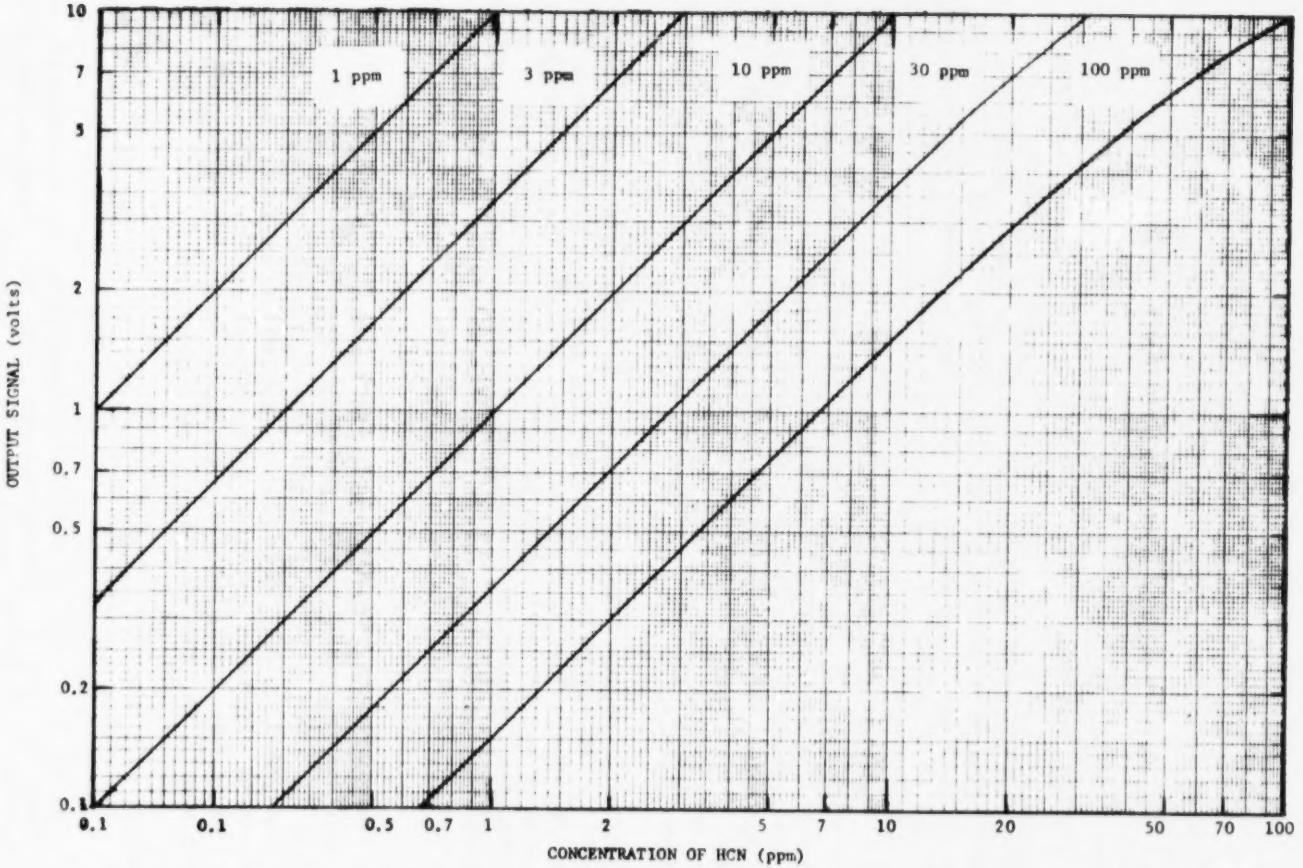

Figure 9. Log-log plots of the output signal vs HCN concentration for the 5 different sensitivity ranges. Concentrations below 10 ppm can be determined directly from the output signal or the panel meter.

The noise level of each instrument was measured by recording the output signal with a strip chart recorder. The sample cell was filled with N_2, and the recording was made for 10 minutes at each of two different time constants: 10 sec. and 3 sec. Table 1 summarizes the rms noise levels (expressed in ppm of HCN) estimated from these recorder tracings.

Flushing gas through the multiple-pass sample cell at rates up to approximately 10 lpm does not significantly increase the noise level. Even higher flow rates may be usable without increasing the noise level, but they have not checked.

TABLE 1 RMS NOISE MEASUREMENTS EXPRESSED IN PPM OF HCN

Instrument No.	3 Sec Time Constant	10 Sec Time Constant
1	0.015	0.012
2	0.010	0.007
3	0.007	0.005

A small drift in the zero-setting (output signal with no absorbing gas in the sample cell) appears to be correlated to filling the detector with liquid nitrogen. Slight shifts in the grating assembly due to temperature differences apparently lead to very slight changes in the spectral bandpass, which in turn, cause shifts in the zero-setting. The drift can be minimized by keeping the detector cooled and not filling it with liquid N_2 to within 1" of the top. If these precautionary procedures are followed, the drift in zero-setting can be reduced to less than 0.2 ppm of HCN per hour.

INTERFERENCE

Table 2 summarizes typical interferences by several gas species that occur in automotive exhaust. The second column gives the concentration of the interfering gas species in a typical sample studied. All interference test samples were at 1 atm total pressure. The average absorptance $\bar{A}$, given in the third

TABLE 2. TYPICAL INTERFERENCE DATA

Gas	Concentration (ppm)	$\bar{A}$	Interference Error (ppm of HCN)	Discrimination Ratio
H_2O	6,000	0.03	+0.38	+15,800:1
H_2O	13,000	0.06	+0.60	+21,700:1
H_2O	25,500	0.11	+0.39	+65,400:1
CO_2	60,000	0.009	-0.12	-500,000:1
NH_3(ammonia)	386	0.052	-0.54	-715:1
CH_4(methane)	3860	0.0015	0.01	> 386,000:1
C_2H_2(acetylene	83	0.032	-0.13	-640:1
C_2H_2	340	0.122	+0.00	∞
C_2H_2	682	0.227	+0.94	+730:1
C_2H_4(ethylene	3860	0.003	-0.04	- 96,500:1
C_2H_6(ethane)	3860	0.017	+0.015	+260,000:1
C_3H_8(propane)	3860	0.217	-0.036	-107,000:1
C_4H_{10}(butane)	3860	0.115	-0.37	- 10,400:1

column, was determined from $(I_o-I_s)/I_o$, where I_s and I_o are the 360 Hz input signals observed with the sample in and the sample out, respectively. The interference, or false signal, produced by each sample appears in the fourth column. The discrimination ratio, D.R., given in the fifth column, represents the ratio between the concentration of an interfering gas and the concentration of HCN required to produce the same output signal. A negative value of D.R. indicates that the interfering gas produces a negative output signal. Note that propane absorbs significantly, but it does not produce a significant interference signal. This indicates that there is little correlation between the spectral structures of propane and of the HCN in the GFC.

It is unlikely that any of the gases listed in Table 2 would occur in concentrations high enough to produce significant interference, except for H_2O, CO_2, NH_3 and C_2H_2. The interference by CO_2 or NH_3 is nearly proportional to the concentration of the gas; therefore, the discrimination ratio for each of these two gases is essentially independent of the concentration. In most cases the interference by NH_3 is probably negligible, but a small correction may be needed if the concentration of this gas is unusually high. The correction for CO_2 interference usually corresponds to less than 0.1 ppm of HCN. The interference by C_2H_2 or H_2O is not directly proportional to the gas concentration. of each of these gases is provided for each instrument. Interference by H_2O is positive for all H_2O concentrations below approximately 3% (30,000 ppm). The interference increases with increasing H_2O concentration up to approximately 13,000 ppm; as the concentration increases further, the interference decreases. Interference by C_2H_2 is negative for small concentrations then becomes positive for higher concentrations.

The most serious interference results from H_2O. The concentration of this gas is measured by the H_2O monitor, making it possible to account for the interference by using previously obtained interference data on $H_2O + N_2$ mixtures. The very small amount of interference by CO_2 can be accounted for from the known discrimination ratio and the concentration, which is usually known accurately enough for this purpose. In situations when the NH_3 or C_2H_2 concentration is usually high, it may be necessary to measure the concentration of the gases so their interferences can be accounted for accurately.

GAS HANDLING

Measurements of the HCN concentration can be made either while a sample is stationary in the sample cell or while it is flowing. If measurements are to be made on a stationary sample, checks should be made to see if a significant amount of the HCN adsorbs on the walls of the incoming-gas lines or the sample cell. Adsorption depletes some of the HCN vapor from the mixture, causing the instrument output signal to be lower than it would be in the absence of adsorption. Adsorption may take place for several minutes after a sample has been introduced into the cell. The continuing adsorption results in a decrease in the output signal. Errors due to adsorption can be reduced by pre-conditioning the gas lines and cell by filling them for several minutes with a sample that contains approximately the same HCN concentration as the sample to be measured. This mixture can then be flushed out by the sample to be measured.

If a sample of high HCN concentration has been in the sample cell, care must be exercised to avoid errors in the next sample if its HCN concentration is much lower than the original sample. In this case, HCN adsorbed on the walls from the original sample may come off the walls and cause an erroneously high reading.

It is recommended that samples be flushed through the cell at 5-10 lpm if enough sample is available. If only a limited amount of sample gas is available, the cell can be preconditioned to reduce errors due to adsorption. No significant errors are being caused by adsorption if the output signal is essentially constant while the flushing rate varies by 50% to 100%.

False output signals corresponding to a few tenths of a ppm of HCN may result while a zero gas is being flushed from the cell with a sample of exhaust gas. A false signal may also occur during the opposite flushing process. These false signals may occur even if neither of the two gases would produce a signal if sampled separately. The signals are apparently due to the difference in the indices of refraction of the two gases. When the gases are not mixed uniformly in the sample cell, the difference in indices causes a slight shift of the monitoring beam where it enters the grating assembly. A slight shift in the zero-setting results. When one of the gases has completely displaced the other one, the false signal disappears and the output signal represents the HCN concentration in the sample cell.

A sample of gas in the cell is approximately 85% flushed out by another gas when the volume of the incoming gas flushed through is 3.7 liters, the volume of the sample cell. When twice the cell volume has been flushed through, between 98 and 99% of the original gas has been removed.

SECTION 9

CONVERSION OF THE VERSATILE GAS-FILTER CORRELATION SPECTROMETER

This section describes the tests performed as the first phase of the program on the versatile gas-filter correlation spectrometer and the conversion of the spectrometer for use as an HCN analyzer. The spectrometer has been described in detail in a previous report[1]. Locations of the components discussed below are shown in the optical diagram in Figure 1 of the same report, along with definitions and discussions of the operating principles and the important instrument parameters.

The work performed during this first phase of the program served two purposes. The first was to perform the tests required to determined an optimum set of instrument parameters and to determine the performance that could be expected from gas-filter cell instruments built specifically for use as HCN analyzers. Conversion of the EPA - owned versatile gas-filter correlation spectrometer for use as an HCN analyzer constituted the second task of the first phase. After the spectrometer was converted, it was returned to the EPA to use in tests on automotive exhaust until three new instruments designed specifically as HCN monitors were built and tested.

DETERMINATION OF INSTRUMENT PARAMETERS

The relatively strong HCN band centered near 3312 cm^{-1} (3μm) was selected instead of the stronger band near 712 cm^{-1} (14μm). Serious interference by CO_2 could be expected if the lower wavenumber band were used because of the strong absorption lines of this gas in the region of the HCN band. In addition, convenient window materials are not available for the low wavenumber region.

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1. Burch, D.E., F. J. Gates, D.A. Gryvnak and J. D. Pembrook. "Versatile Gas Filter Correlation Spectrometer," Prepared by Aeronutronic Ford Corporation under Contract No. 68-02-1227. EPA Report No. 600/2-75-024, June 1975.

The 300 line/mm grating, the Nernst glower source, and the liquid-nitrogen-cooled PbS detector were installed in the versatile spectrometer. Various sample cell lengths were employed during the tests, but the multiple-pass sample cell was adjusted to 28 passes (L = 28m) before the instrument was calibrated and returned to the EPA. By using a variety of grids in the retroreflector-grid assembly and by adjusting the grating position, we were able to use many different spectral b ndpasses for the tests. The most important factor in the choice of the spectral bandpass is the need to minimize the interference by H_2O, C_2H_2 and NH_3. As explained in Section 5, use of the strongest portion of the 3μm HCN band is not practical because of excessive interference by C_2H_2 and NH_3. Bandpasses of many different widths and center positions were tried. The bandpass selected for the versatile spectrometer extends from approximately 3338 cm^{-1} to 3356 cm^{-1}. The minimum width of the bandpass is determined by the amount of radiant energy required to produce an acceptable ratio of the detector signal to noise.

While assembling the 3 new instruments built under Phase II, we determined that somewhat better discrimination could be obtained by using a grid with two openings that produces the spectral transmittance function illustrated in Figure 6. Because of the improved detectors used in the new instruments, we were able to achieve a satisfactory signal-to-noise ratio while employing this bandpass, which is narrower than the one employed in the converted versatile spectrometer.

Epoxy cement used to seal windows to the body of the gas-filter cell was found to decompose because of reaction with HCN in the cell. Leaks developed in the seal within a few weeks after a cell was filled. This problem was overcome by fusing quartz windows to the quartz cell body. A one-half atmosphere mixture of 15.8% HCN, 6.7% C_2H_2 and 77.5% N_3 was introduced into the 1.1 cm long cell through a small-bore tubing, and the cell was sealed by filling the tubing with epoxy cement. Only approximately 0.1 mm^2 of epoxy is in contact with the HCN vapor. Infrared spectrum of the HCN in the cell have been scanned periodically and compared with a spectrum scanned a few days after the cell was filled. The comparisons indicate that the amount of HCN in the cell has not changed by more than 10% in nearly a year. The change, if any, may be much less than this amount.

Discrimination against C_2H_2 and NH_3 is improved further by a "series" cell in the optical path near the entrance window of the multiple-pass sample cell. The 500 torr of C_2H_2 and 250 torr of NH_3 in this 5-cm long series cell absorb much of the energy near the centers of the strong absorption line of these gases. Thus, adding either of these two gases to the sample cell has less effect on the detector signal than it would have without the series cell in place.

After inserting the series cell, C_2H_2 and NH_3 still interfered slightly. The NH_3 interfered positively, i.e., it caused the output signal to be too large. This interference was reduced further by placing an "attenuator cell" in the alternator section of the instrument in the position normally occupied by a neutral-density attenuator. The 1-cm long attenuator contains 450 torr of NH_3. Negative interference by C_2H_2 was greatly reduced by the 25 torr of C_2H_2 added to the HCN in the GFC. With this combination of gas-filter cell,

series cell and attenuator cell, the interference signal caused by C_2H_2 and NH_3 at the highest concentrations normally found in automotive exhaust corresponds to less than the minimum detectable concentration of HCN.

A slight interference by H_2O in the sample is accounted for in the same manner as in the three monitors described in the first 8 sections of this report. An H_2O monitor similar to the one described in Section 7 measures the H_2O concentrations.

SECTION 10

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